

INFRARED SPECTRA OF MOLECULES AND MATERIALS  
OF ASTROPHYSICAL INTEREST

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## INTRODUCTION

In the first progress report we reported the vibrational study of tetradeuterated hydrazine. Progress report number two dealt with the vibrational spectrum of matrix isolated  $\text{CH}_3\text{NH}_2$  and the infrared spectra of  $\text{CH}_3\text{NH}_2$ ,  $\text{CD}_3\text{NH}_2$  and  $\text{CD}_3\text{ND}_2$  in the solid phases. We have continued our studies of methylamine and we recorded the vibrational spectra of matrix isolated  $\text{CD}_3\text{NH}_2$  and  $\text{CD}_3\text{ND}_2$ . We have analyzed the data and we are currently writing up the results for publication. Therefore, since a paper will be submitted shortly for publication, we are going to omit a detailed discussion of this phase of our studies at this time.

We are continuing our studies of molecules which could be possible constituents of the Jovian atmospheres. Gerard P. Kuiper<sup>1</sup> in his book on The Atmospheres of the Earth and Planets has pointed out that the Jovian atmospheres are expected to contain  $\text{H}_2$ , He, Ne,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , Ar and possibly  $\text{SiH}_4$ . He has also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below  $120^\circ\text{C}$  [see Table 8, pg. 349-350]. He has also pointed out that until more is known about the atmospheres of the planets it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work. In the initiation of our work on the infrared spectra of molecules of astrophysical interest, we studied

hydrazine and methylamine. However, there are several other small molecules containing hydrogen, carbon, and nitrogen which also should be possible constituents of the reducing atmospheres. Similarly, phosphine, silane and hydrogen sulfide have been proposed as possible constituents of the Jovian planets as well as the hydrocarbons acetylene, ethylene, and ethane. If one accepts these materials as possible constituents, then due to the probability of photochemical reactions, other such molecules as ethylsilane, methylphosphine, vinylsilane, isothiocyanic acid as well as others are also possible constituents of these atmospheres. It is true that some of the proposed compounds will also polymerize under ultraviolet irradiation, but the planets with hot bases, for example Jupiter and possibly Saturn, could rebuild such molecules that had been destroyed photochemically. The infrared spectra of many of the above mentioned molecules have not been studied or the results are so conflicting that convincing vibrational assignments are not possible.

Phosphorus, sulfur and fluorine all have rather large natural cosmic abundances<sup>2</sup> and the molecule  $\text{SPF}_3$  boils at  $-52^\circ\text{C}$  and is rather stable. The Raman data on this molecule had been studied by Dewaulle and Francois<sup>3</sup> and normal coordinate calculations had been performed by Nagarajan<sup>4</sup> and Ziomek and Piotrowski<sup>5</sup>. However, the accepted vibrational assignment<sup>6</sup> for this molecule proposes a P=S stretching and a P-F symmetrical stretching

vibrations which were incompatible with those found for other fluoride-sulfur containing compounds. Therefore, we undertook the investigation of the infrared spectrum of  $\text{SPF}_3$  from 4000 to  $33\text{ cm}^{-1}$  in order to try to resolve the discrepancy. As expected, the band at  $874\text{ cm}^{-1}$  previously reported in the Raman study, was found to be an impurity. This band had been assigned as the P=S stretching vibration. Since the band was found not to belong to the  $\text{SPF}_3$  molecule, it was necessary to reassign the fundamental modes of this molecule. The infrared spectrum of  $\text{SPF}_3$  shows two bands in the P-F stretching region, one centered at  $981\text{ cm}^{-1}$  and the other at  $945\text{ cm}^{-1}$ . The former one has a band contour expected for a parallel fundamental and can be confidently assigned as the  $\text{PF}_3$  symmetric stretching vibration. The band contours of the perpendicular bands are all expected to be different because of the zeta values. However, the Raman spectrum of  $\text{SPF}_3$  shows the  $945\text{ cm}^{-1}$  band to be definitely polarized, and it is, thus, assigned as the  $\text{PF}_3$  antisymmetric stretching vibration. The P=S stretching vibration is then assigned to the parallel band centered at  $695\text{ cm}^{-1}$ . The assignment of the other three bands agreed with that given in the earlier Raman work<sup>3</sup>. Of course, the thermodynamic properties calculated earlier<sup>5</sup> by using the incorrect vibration frequencies are now invalid and we have calculated new values based upon our vibrational assignment. We have also investigated the vibrational spectra of  $\text{SPF}_2\text{Cl}$  (boiling point  $6^\circ\text{C}$ ) and  $\text{SPFCl}_2$  (boiling point  $64\text{-}65^\circ\text{C}$ ) and

vibrational assignments have been made. No previous infrared studies have been reported for these molecules. We have submitted this work for publication in the Journal of Chemical Physics and a preprint of the submitted paper is enclosed in the appendices of this report.

Very recently, infrared spectroscopic<sup>7</sup> studies of the vacuum ultraviolet photolysis products of carbon dioxide at 77°K was made and a molecular species was identified as carbon trioxide. Isotopic experiments involving C<sup>13</sup> and O<sup>18</sup> were carried out and a planar trigonal symmetry was confirmed<sup>7</sup>. The fundamental frequencies for various isotopic species were assigned on the basis of D<sub>3h</sub> symmetry and force constants, assuming a Urey-Bradley force field, were calculated by Clutter et al.(7). Raper and De Mare(8) also reported that carbon trioxide was formed as an intermediate in their photolysis reaction between electronically excited diatomic oxygen and carbon monoxide.

As a continuation of our utilization of vibrational data to determine thermodynamic properties, we have calculated the mean amplitudes of vibration, the thermodynamic functions and the molecular polarizabilities of a series of mixed phosphorus-halogen compounds of the type PX<sub>2</sub>Y where X is fluoride, chloride or bromide and Y is also fluoride, chloride or bromide. These calculations have been submitted for publication and presented in this report as part III of the appendices.

### FUTURE WORK

The investigation of the vibrational spectra of molecules which could be possible constituents of the Jovian atmospheres will continue and when desirable the data will be used to calculate thermodynamic properties, force constants and other useful molecular properties.

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